LAMQS, EDXRF and SEM analyses of old coins

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Abstract

Physical analyses by Laser Ablation coupled to Mass Quadrupole Spectrometry (LAMQS), Energy Dispersive X-Ray Fluorescence (EDXRF) induced by electron beam and SEM (Scanning Electron Microscopy) morphological investigations have been employed, as not destructive analyses, in order to characterize the surface of different old coins. Gold, silver and bronze coins have been studied to know their superficial patina composition and morphology. In particular LAMQS permitted to investigate the elemental, chemical compounds composition and isotopic ratios without damage the laser irradiated surface.The comparison of similar coins permitted to identify true and fake samples, so as demonstrated for different coins and for a rare silver tetradrachm Greek coins dated 480 - 461 B.C., which has many imitations.

INTRODUCTION

Laser Ablation coupled to Mass Quadrupole Spectrometry (LAMQS) is a new techniques recently used for the deep profile and compositional analysis of different solid materials [1]. Flexible laser conditions (pulse energy, wavelength, spot size, incidence angle, etc.) and relative speed of analysis are advantages of the method, which make this technique attractive for depth profile analysis, for cleaning and for non-disruptive surface analysis. The energy of the laser pulses is deposited onto the analyzed surface to induce desorption and vaporization of the most superficial mono-layers of the sample material. The vapor is then ionized and analyzed in mass by a suitable quadrupole spectrometer.

The use of LAMQS, of the complementary analyses based on the Energy Dispersive X-ray fluorescence (EDX) induced by electron beam and by Scanning Electron Microscopy (SEM), may represent an useful team techniques to investigate with success on the morphology, chemical composition, isotopic ratios and elemental maps of solid sample surfaces. LAMQS, EDX and SEM represent three non-destructive analysis techniques useful in the field of cultural heritage for analysis of little precious pieces analyzable in high vacuum conditions.

LAMQS gives information on the developed gas phase in terms of atomic mass units, chemical compounds and isotopic species. A preliminary calibration of the LAMQS permits to use it as a micro-invasive analytical method of the solid surface. EDX gives the elemental composition of the first superficial layers irradiated with about 20 keV electron beam permitting to evince the elemental map distribution. SEM gives the morphology of the investigated surfaces at low and high magnification [2].

In this work, these physical techniques have been applied to the surface analysis of different old coins. Gold, silver and bronze coins have been studied to know their superficial patina composition and morphology. The analytical team techniques permits to evince the surface composition in relation with the geographic area of the coins realization and of the old mineral used for the coin production. Coins are kindly furnished by Dipartimento di Lettere e Filosofia dell'Università di Messina (Italy).
The results of the techniques permit also to compare the patina composition of different coins and to distinguish fake coins from true ones as will be discussed in the following

EXPERIMENTAL SECTION

A Nd:Yag laser operating at 1064 nm fundamental wavelength, 3 ns pulse width, 1-150 mJ pulse energy, single pulse or 1-10 Hz repetition rate, was employed. Laser spot on the target was large (about 30 mm^2) in order to reduce the intensity avoiding any visible surface damage.

The coins were placed in a vacuum chamber holder at 10^{-7} mbar pressure.

In order to evaluate the ablation yield (number of removed atoms/pulse), the laser ablation technique was calibrated with standard-samples having a bulk composition similar to that of the ancient coins. Gold, silver and copper targets were laser irradiated to this aim and the crater volume produced by the removed atoms was measured with a surface profiler (Tencor P10) with 10 mm maximum surface sweep and 1nm depth resolution.

Fig. 1 shows the measurements of the ablation yield as a function of the laser fluence for the three calibration targets using 100 mJ laser pulse energy. A threshold below which no ablation occurs is evident [3]. Above the threshold, the ablation yield increases linearly with the laser fluence. Thus the measure of the laser fluence permits to control the crater depth. Generally the fluence was maintained just above the ablation threshold and the removing depth below 10 nm/pulse so that the ablation technique can be considered not-destructive (micro-invasive) using a low number of laser shots.

Before to apply the LAMQS technique, the coins have been analysed by using the EDX spectroscopy induced by 20 keV electrons and by a scanning electron microscope (SEM) in order to know the morphology, the elements present in the first micron depth (electron range) of the patina coin and their map distribution.

Successively, LAMQS technique was employed with a mass quadrupole spectrometer (MQS), Pfeiffer Vacuum-prisma 200, with 1-200 amu mass range, a mass resolution less than 1 amu and a sensitivity less than 1 ppm (at 40 amu). LAMQS data acquisition were performed at 1 Hz repetition rate and for a time interval lower than 40 sec.

Three kind of coins, of special interest in the Archaeological field and based on bronze, silver and gold alloys, were investigated. The first was a bronze coins coming from the Alexandria Egyptian sites; it is dated VI-VII sec A.C.. The second was a silver tetradrachm Greek coins coming from Sicily; it is dated 480 - 461 B.C.. The third was a Byzantine gold coin; it is dated 500 A.C..

RESULTS

Fig. 2 shows the EDX spectra relative to the three investigated coins and, in the inset, the corresponding coin photos.

EDX spectra give the elemental composition of the patina coins. The gold coin has high gold concentration (about 98%) and trace concentrations of the following elements: Fe, Tl, Rb, Ca, K, Si, Al, O e C. The silver coin has high Ag concentration (about 98%) and trace elements of C, O, Mg, S, Cl, Fe, Cu and Ni. The bronze coin has an elemental composition consisting of Cu (77%), Fe (6%), Sn (9.5%) and Pb (7,5%), as a typical alloy of old bronze, and, in the patina layers, contains also the following elements O, Cl, S, Si.

LAMQS distinguishes different compounds present in the coin patinas and laser-evaporated in the vacuum chamber. A typical LAMQS spectrum of some Fe compounds vs. the laser irradiation time is reported in Fig. 3a. Fe, FeCl, FeO and FeS are detectable during the laser ablation. The MQS yield (difference between the signal at laser on and the background at laser off) is proportional to the concentration of the detected mass present in the patina ablated layers.

Different bronze coins show a different content in the Fe compounds. Other compounds typical of bronze coins are oxides, chlorides and sulphured of many elements. The bronze coin patina contains many compounds containing oxygen, such as FeO, CuO and SnO, chlorine, as FeCl, CuCl, and SnCl and sulphur, as FeS, CuS and SnS. Such chemical structures are correlated to the environment and to the mineral of the provenience sites, ion fact similar coins have similar composition.

Fig. 3b reports the MQS detection of the stable Fe^{54}, Fe^{56} and Fe^{57} isotopes emitted in vacuum during the laser ablation of the bronze coin patina. The spectra permit to calculate the relative isotopic ratio, typical of the analyzed coin. The isotopic ratios of the most representative elements of the bronze, typical of the used mineral, shows the following isotopic ratios:

Cu^{63}/Cu^{65} = 2.18; Sn^{120}/Sn^{118} = 1.30; Pb^{208}/Pb^{205} = 2.10; Fe^{56}/Fe^{54} = 16.00.

These values are about 2-3% different from the expected abundance isotopic ratios of 2.24, 1.35, 2.17 and 15.67, respectively [4].

Similar investigations have been applied to the other studied coins. Measurements have permitted to evince the main elemental compounds presents in the patina and to measure their relative isotopic ratios. Such data represent a characteristic imprinting of the mineral used to prepare the coin.

For example the silver coin patina contains AgO, AgCl and AgS and has an isotopic ratio Ag^{107}/Ag^{109} = 1.10. The LAMQS comparison of the silver tetradrachm greek coin with an imitation silver fake has demonstrated that the patina composition and the isotopic ratios are significantly different. The fake sample contains a lower concentrations of AgO and AgCl with respect to the true coin and has nearly absence of AgS. The isotopic ratio is more similar to the expected abundance value of Ag^{107}/Ag^{109} = 1.076. Moreover, SEM investigations demonstrated that the fake low relief morphology is typical of recent manufactured silver and not of very old metal, showing high wear and very smoothed low relief, as reported in a previous our article [5].

Due to the low reactivity of the gold, the chemical compounds in the gold patina coin are present at lower concentrations. All surfaces shows a significant presence of absorbed hydrogen, oxygen, nitrogen and carbon. However such elements have a trace concentration in the gold Byzantine patina coin.

DISCUSSION AND CONCLUSIONS

The techniques used for the present work, i.e. EDX, LAMQS and SEM, have been extensively used in determining the compositional content of the alloys used by ancient mints and represent powerful tools for the microscopic characterization of metallic samples. Because the techniques are not invasive, only the surface patina of the investigated coins was analysed. However, the elements, the chemical compounds and the isotopic concentrations are well representative of the original mineral used and of the environmental place were the coins were saved for tens of centuries. This characterization seems to be a identity card for the coin and permits to correlate the patina composition with the environment and the mineral used to build the coin. In this sense different analysis permits to identify similar coins with a similar origin and to furnish interesting data for argumentations in archaeological field.

Fake samples become easily distinguishable from the true ones because their patina thickness is lower, their composition and isotopic ratio are different and the morphology may show different properties (wear, micro and macro-fractures, porosity, element and micro-particle insertions,…).

In conclusion, due to the microscopic and near not-invasive LAMQS analysis, the presented techniques becoming of high interest for numismatics as well as for forensic and historical investigations.

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